The Preparation and Utility of Ethyl 2-(5′-*O*-t-Butyldimethylsilyl-2′,3′-*O*-isopropylidene-β-D-ribofuranosyl)propenoate as a Key Intermediate for *C*-Nucleoside Synthesis

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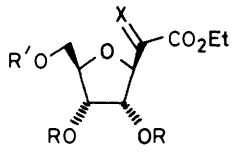
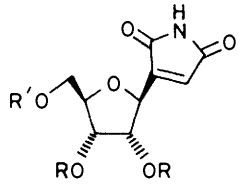
We describe a short route from D-ribose to compounds (**Ib**) and (**Ic**), which can be converted into the showdomycin derivative (**IIb**) and certain novel *C*-nucleosides. A key step in this synthetic sequence involved a stereoselective cyclisation facilitated by the use of phenylselenenyl chloride.

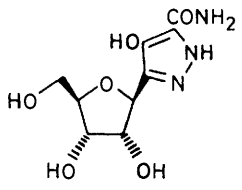
The keto-esters (**Ia**) and (**Ic**) have been utilised as intermediates in three syntheses[1] of the structurally unique *Streptomyces* metabolite showdomycin (**IIa**),[2] and (**Ia**; R = R′ = Ac) has also been employed in a synthesis[3] of the *C*-nucleoside pyrazomycin (**III**).[4] The proven synthetic potential of these intermediates prompted us to consider an alternative synthesis, and our five-step synthesis commences with D-ribose and allows obtention of the unsaturated ester (**Ib**) and then provides (**Ic**) after ozonolysis.



(**I**) **a**; X = O, R = R′ = benzoyl (*or* acetyl)
b; X = CH_2, R = acetonide, R′ = $SiMe_2Bu^t$
c; X = O, R = acetonide, R′ = $SiMe_2Bu^t$

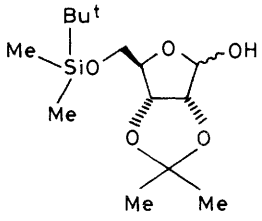


(**II**) **a**; R = R′ = H
(**II**) **b**; R = acetonide, R′ = $SiMe_2Bu^t$

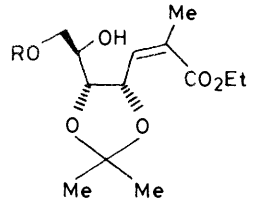


(**III**)

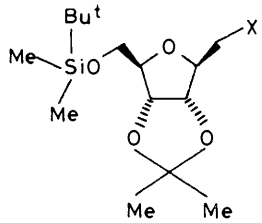
D-(−)-Ribose was converted in two stages into the 2,3-*O*-isopropylidene-5-*O*-t-butyldimethylsilyl derivative (**IV**), and this then reacted with 1-ethoxycarbonylethylidene(triphenyl)-phosphorane in dichloromethane at ambient temperature to yield the acyclic product (**Va**).† There is much precedent for the formation of both cyclic and acyclic products in Wittig reactions with D-ribose.[5] We confirmed Moffatt's finding that reactions involving stabilised ylides in acetonitrile at reflux over several hours provide cyclic products (**VI**), usually with excellent stereoselectivity (β : α anomeric ratios in the range 25 to 50 : 1). However, by using dichloromethane at room temperature we were able to maximise formation of the desired product (**Va**) [80—90% from (**IV**)]. Ring closure was then effected using



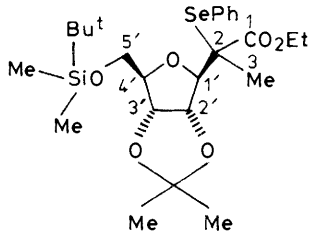
(**IV**)



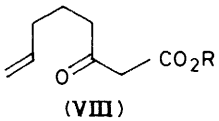
(**V**) **a**; R = $SiMe_2Bu^t$
(**V**) **b**; R = H



(**VI**) X = CO_2Me *or* CN



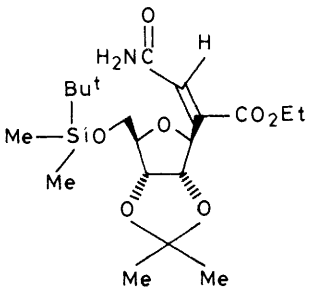
(**VII**)



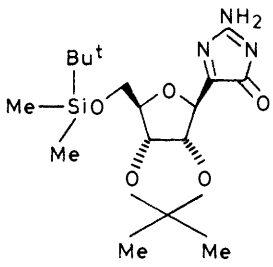
(**VIII**)

phenylselenenyl chloride in dichloromethane (−78 °C to room temperature) to produce the phenylseleno derivative (**VII**) (40% yield after flash chromatography), which was subsequently shown to have β-stereochemistry. None of the alternative α-substituted product was obtained, but some unchanged starting material was recovered (29%). Many research groups have employed selenium compounds in cyclisations, and the recent use by Nicolaou to form polysubstituted tetrahydrofurans and bicyclic systems,[6] and by Ley *et al.*[7] who studied the cyclisation of alkenyl-substituted β-oxo-esters, *e.g.* (**VIII**), are representative; but to our knowledge this is the first time that a selenium compound has been used to effect stereoselective cyclisation in the carbohydrate area. Any explanation for the excellent stereoselectivity observed must take into account the finding that the process is just as stereoselective when the 5-hydroxy group of ribose is unprotected [*i.e.* using (**Vb**) as substrate]. It appears that the isopropylidene group provides enough steric hindrance by itself to ensure formation of the *cis*-1,4-disubstituted ribose derivative, and a similar result has already been mentioned in connection with the Wittig reactions in refluxing acetonitrile. That the β-stereochemistry was present at C-1′ (ribose numbering) was evident once compound (**VII**) had been converted into the α-methylene ester (**Ib**) by treatment with

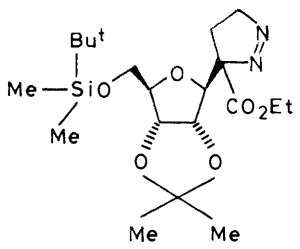
† The major product has been assigned *cis*-stereochemistry on the basis of Moffatt's results,[5] and because the allylic coupling between the methyl protons and 3-H was 2 Hz rather than 1 Hz (for a good discussion of coupling in similar systems see S. Sternhell, *Rev. Pure Appl. Chem.*, 1964, **14**, 15).



(IX)



(X)



(XI)

hydrogen peroxide at 0 °C. This *syn* elimination of phenylselenenic acid proceeded in almost quantitative yield. The ^{13}C n.m.r. data for this compound were fully consistent with the assigned stereochemistry, and in particular the chemical shifts of the isopropylidene methyls and the quaternary carbon atom of the isopropylidene group (δ_C 25.651, 27.625, and 113.793 p.p.m. respectively) were in agreement with values provided by Moffatt,[5] Buchanan,[8] and Klein[9] for 1β-substituted ribose derivatives. In addition, the ^1H n.m.r. signals (at 100 MHz) for the isopropylidene methyls appeared at δ 1.34 and 1.57 ($\Delta\delta > 20$ Hz) which is also suggestive of β-stereochemistry; and $J_{3'4'}$ was 4 Hz (usually *ca.* 0 Hz for α-forms). Finally, compound (**Ib**) was converted into the known showdomycin intermediate (**IIb**). This was achieved by firstly converting (**Ib**) into the keto-ester (**Ic**) (ozonolysis in methanol at −78 °C, then treatment with dimethyl sulphide),[10] and then reaction of the product with carbamoylmethylene(triphenyl)phosphorane to yield the ester amide (**IX**) [33% yield overall from (**Ib**)]. It is interesting to note that in the similar sequence reported by Just and his co-workers,[1] which used the corresponding methyl ester, spontaneous cyclisation occurred at this stage to produce the showdomycin derivative (**IIb**). Our ethyl ester required an acid catalyst and refluxing benzene to cause isomerisation and ring closure, forming the same compound (**IIb**). Spectra obtained with this product were identical in every respect with those kindly provided by Professor Just, and we thus turned our attention to the formation of novel *C*-nucleosides *via* the same key intermediates.

Reaction of (**Ic**) with guanidine allowed obtention of the imidazolone (**X**), while a cycloaddition between (**Ib**) and diazomethane yielded the dihydropyrazole (**XI**). This latter process was particularly efficient, and pure crystalline cycloadduct was obtained in 81% yield. Deprotection of both compounds was achieved using aqueous trifluoroacetic acid, and the final products were isolated as their hydrogen chloride salts, which were submitted for biological testing.

These examples give further evidence of the utility of (**Ic**) in *C*-nucleoside synthesis, but also indicate that the novel compound (**Ib**) may also provide ready access to a range of novel *C*-nucleosides. In particular, the production of this species from the ribose derivative (**IV**) is efficient (three steps: 85%, 65% with allowance for recovered starting material, and 97%), and can be carried out on the multigramme scale.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 157 double-beam grating spectrophotometer (liquid films for oils and Nujol mulls for solids); ^1H n.m.r. spectra were recorded with a Varian T-60 (60 MHz), Varian HA 100 (100 MHz) instruments, or with a Perkin-Elmer R34 (220 MHz) instrument (tetramethylsilane as internal standard); ^{13}C n.m.r. spectra were recorded at the City of London Polytechnic on a Jeol FX90Q (90 MHz) instrument; and mass spectra were recorded on an A.E.I. MS12 spectrometer. Kieselgel $GF_{254+354}$(Merck) was used for analytical t.l.c., and flash chromatography was performed with Merck silica gel (230—400 mesh). Organic solvents were distilled from calcium hydride when required anhydrous. Light petroleum refers to the fraction boiling in the range 40–60 °C.

5-O-t-*Butyldimethylsilyl*-2,3-O-*isopropylidene*-D-*ribofuranose* (**IV**).—A solution of 2,3-*O*-isopropylidene-D-ribose (3.87 g, 20.4 mmol), imidazole (2.1 g), and t-butyldimethylsilyl chloride (3.11 g, 20.7 mmol) in dimethylformamide (DMF) (70 ml) was stirred at room temperature for 19 h. The bulk of the DMF was removed under reduced pressure, and the crude product was then purified by flash chromatography using light petroleum–diethyl ether (3:2) as eluant to afford (**IV**) as a white crystalline solid (4.1 g, 66%), m.p. 47 °C; R_F 0.41 [light petroleum–diethyl ether 3:2)]; $\nu_{max.}$ 3 350, 1 460, 1 375, 1 240, 1 210, 1 160, 1 085, 1 070, 1 040, 985, 935, 875, 860, 835, and 775 cm^{-1}; $\delta_H(CDCl_3)$ 0.15 (6 H, s, $SiMe_2$), 0.95 (9 H, s, $SiBu^t$), 1.32 and 1.50 (together 6 H, 2 s, CMe_2), 3.75 (2 H, d, *J* 2.5 Hz, OCH_2), 4.35 (1 H, m, $J_{4,5}$ 2.5 Hz, 4-H), 4.5 (1 H, d, $J_{2,3}$ 6 Hz, 3-H), 4.6 (1 H, d, *J* 11 Hz, OH), 4.7 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), and 5.25 (1 H, d, *J* 11 Hz, 1-H) (Found: C, 55.4; H, 9.2. Calc. for $C_{14}H_{28}O_5Si$: C, 55.23; H, 9.27%).

Ethyl (4S,5R,6R)-7-t-*Butyldimethylsilyloxy*-6-*hydroxy*-4,5-O-*isopropylidene*-2-*methylhept*-2-*enoate* (**Va**).—A solution of compound (**IV**) (3.33 g, 10.96 mmol) and 1-ethoxycarbonylethylidene(triphenyl)phosphorane (5.43 g, 15 mmol) in dichloromethane (50 ml) was refluxed for 6 h under nitrogen, and then stirred at room temperature for a further 60 h. The homogeneous reaction mixture was concentrated and purified by flash chromatography using light petroleum–diethyl ether (2:1) as eluant to give an oil (3.62 g, 85%) which was primarily the (*Z*)-ester (**Va**), but which contained small amounts of the (*E*)-isomer (at least 9:1), R_F 0.43 [light petroleum–diethyl ether (3:2)]; $\nu_{max.}$ 3 500, 2 990, 2 960, 2 940, 2 860, 1 720, 1 660, 1 475, 1 465, 1 385, 1 370, 1 320, 1 250, 1 220, 1 170, 1 120, 1 060, 910, 840, and 780 cm^{-1}; $\delta_H(CDCl_3)$ 0.1 (6 H, s, $SiMe_2$), 0.9 (9 H, s, $SiBu^t$), 1.3 (3 H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 1.35 and 1.45 (together 6 H, 2 s CMe_2), 1.9 (3 H, d, *J* 2 Hz, 2-Me), 2.4 (1 H, br s, OH), 3.55—3.99 (3 H, m, 6-H and 7-H_2), 4.1 (1 H, m, 5-H), 4.2 (2 H, q, *J* 7 Hz, CO_2CH_2), 5.0 (1 H, dd, *J* 9 and 6 Hz, 4-H), and 6.7 (1 H, dq, *J* 9 and 2 Hz, 3-H) (Found: C, 58.65; H, 9.4. Calc. for $C_{19}H_{36}O_6Si$: C, 58.73; H, 9.34%).

Ethyl 2-(5′-O-*t-Butyldimethylsilyl*-2′,3′-O-*isopropylidene*-β-D-*ribofuranosyl*)-2-(*phenylseleno*)*propionate* (**VII**).—A solution of compound (**Va**) (3.46 g, 8.9 mmol) in dichloromethane (200 ml, dried over 4A sieves) was stirred with anhydrous potassium carbonate (6.9 g, finely divided) at −78 °C under nitrogen. Phenylselenenyl chloride (2.04 g, 10.7 mmol) was added in portions, and the temperature was maintained at −78 °C following completion of the addition. The mixture was then allowed to warm to room temperature, and stirred vigorously for 48 h. A solution of aqueous sodium hydrogen carbonate was then added, and the organic layer was washed successively with a further aliquot of aqueous sodium hydrogen carbonate and then brine. After the organic phase had been dried and concentrated the crude product was purified by flash chromatography using light petroleum–diethyl ether (4:1) as

eluant. The yield of pure oily product (**VII**) was 1.986 g (41%), and *ca.* 1 g of starting material (*ca.* 30%) was also recovered. Compound (**VII**) had R_F 0.45 [light petroleum–diethyl ether (3:1)]; $\nu_{max.}$ 3 060, 2 980, 2 960, 2 860, 1 730, 1 580, 1 475, 1 465, 1 440, 1 385, 1 370, 1 250, 1 220, 1 080, 840, 780, 740, and 695 cm^{-1}; $\delta_H(CDCl_3$; 200 MHz) 0.88 (9 H, s, SiBu^t), 1.14 (3 H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 1.43 and 1.61 (together 6 H, 2 s, CMe_2), 1.5 (3 H, s, 3-H_3), 3.75 (1 H, dd, $J_{5',5''}$ 12 Hz, $J_{5',4'}$ 4.5 Hz, 5'-H), 3.82 (1 H, dd, $J_{5',5''}$ 12, $J_{5'',4'}$ 3.5 Hz, 5'-H), 4.0 (1 H, m, $J_{4',5'}$ 4.5, $J_{4',5''}$ 3.5, $J_{3',4'}$ 5 Hz, 4'-H), 4.06 (2 H, q, *J* 7 Hz, CO_2CH_2), 4.58 (1 H, d, *J* 4.5 Hz, 1'-H), 4.63 (1 H, dd, $J_{3',4'}$ 5, $J_{2',3'}$ 5.5 Hz, 3'-H), 4.83 (1 H, dd, $J_{2',3'}$ 5.5, $J_{1',2'}$ 4.5 Hz, 2'-H), and 7.3—7.8 (5 H, m, Ph); *m/z* (8.7%) ($M^+ - C_4H_9$) 487.1058 ($C_{21}H_{31}O_6SeSi$ requires *m/z* 487.1055).

Ethyl 2-(5'-O-t-*Butyldimethylsilyl*-2',3'-O-*isopropylidene*-β-D-*ribofuranosyl*)*propenoate* (**Ib**).—To a stirred solution of compound (**VII**) (1.74 g, 3.2 mmol) in tetrahydrofuran (THF) (25 ml) and glacial acetic acid (0.5 ml) held at 0 °C was added 30% hydrogen peroxide (2.3 ml, dropwise). The mixture was stirred for 40 min at this temperature, and then 10% aqueous sodium hydrogen carbonate (15 ml) was added, followed by extraction of the product into diethyl ether. The extract was washed with saturated aqueous sodium chloride (2 × 15 ml), dried, and concentrated. Purification by flash chromatography using light petroleum–diethyl ether (4:1) as eluant yielded the acrylate (**Ib**) (1.2 g, 97%) as a pure, oily product, R_F 0.47 [light petroleum–diethyl ether (3:1)]; $[\alpha]_D^{22}$ −7.0° (*c* 1.13 in $CHCl_3$); $\nu_{max.}$ 2 980, 2 960, 2 860, 1 720, 1 635, 1 475, 1 465, 1 380, 1 370, 1 255, 1 080, 835, 775, and 755 cm^{-1}; $\delta_H(CDCl_3)$ 0.88 (9 H, s, Bu^t), 1.3 (3 H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 1.34 and 1.57 (together 6 H, 2 s, CMe_2), 3.62—3.90 (2 H, ddd, $J_{5',5''}$ 12, $J_{5',4'}$ 5 and 4 Hz, 5'-H), 4.05 (1 H, m, $J_{4',5''}$ 4 and 5, $J_{4',3'}$ 4 Hz, 4'-H), 4.24 (2 H, q, *J* 7 Hz, CO_2CH_2), 4.52 (1 H, dd, $J_{2',3'}$ 7, $J_{2',1'}$ 3.3 Hz, 2'-H), 4.62 (1 H, dd, $J_{3',2'}$ 7, $J_{3',4'}$ 4 Hz, 3'-H), 4.8 (1 H, m, $J_{1',2'}$ 3.3, $J_{1',3}$ 1.6 and 1.2 Hz, 1'-H), and 6.0 and 6.26 (together 2 H, 2 m, $=CH_2$); $\delta_C(CDCl_3)$ −5.44 and −5.36 ($SiMe_2$), 14.166 ($CO_2CH_2CH_3$), 18.338 (CMe_3), 25.651 and 27.625 (CMe_2), 25.895 (CMe_3), 60.702 (CO_2CH_2), 63.329 (C-5'), 81.261 (C-1'), 83.103 and 84.918 (C-2' and C-3'), 85.514 (C-4'), 113.793 (CMe_2), 125.657 ($=CH_2$), 139.282 (C-2), and 165.488 p.p.m. (CO_2Et); *m/z* (11.2%) ($M^+ - CH_3$) 371.1891 ($C_{18}H_{31}O_6Si$ requires *m/z* 371.1890).

Ethyl (E)-2-(5'-O-*t-Butyldimethylsilyl*-2',3'-O-*isopropylidene*-β-D-*ribofuranosyl*)-3-*carbamoylpropenoate* (**IX**).—Ozone was passed through a solution of compound (**Ib**) (0.39 g, 1 mmol) in chloroform (25 ml) at −78 °C for 5 min, and excess of ozone was then removed by flushing the flask with nitrogen. Dimethyl sulphide (0.2 ml) was then added, and the reaction mixture was stirred at 0 °C for 10 min, then flushed with nitrogen for a second time. Carbamoylmethylenetriphenylphosphorane (0.383 g, 2.2 mmol) was added and the reaction mixture was stirred at room temperature for 2.5 h before concentration and flash chromatography using diethyl ether as eluant. The pure, oily (*E*)-ester (**IX**) was obtained in 33% overall yield from (**Ib**), and some keto-ester (**Ic**) (0.072 g, 19%) was also recovered unchanged (from the ozonolysis step). Compound (*E*)-(**IX**) had R_F 0.2 (diethyl ether); $[\alpha]_D^{20}$ −28.2° (*c* 1.04 in $CHCl_3$); $\nu_{max.}$ 3 530, 3 490, 3 410, 3 350, 3 180, 2 990, 2 950, 2 930, 2 860, 1 725, 1 690, 1 650, 1 590, 1 470, 1 465, 1 405, 1 385, 1 375, 1 310, 1 250, 1 225, 1 150, 1 075, 975, 855, and 835 cm^{-1}; $\delta_H(CDCl_3)$ 0.88 (9 H, s, SiBu^t), 1.3 (3 H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 1.32 and 1.53 (together 6 H, 2 s, CMe_2), 3.74 (2 H, d, $J_{5',4'}$ 4 Hz, 5'-H_2), 4.1 (1 H, m, 4'-H), 4.28 (2 H, q, *J* 7 Hz, CO_2CH_2), 4.62 (3 H, complex m, 1'-, 2'-, and 3'-H), 6.06 (2 H, br s, NH_2), and 6.27 (1 H, d, *J* 1.3 Hz, 3-H).

2-(5'-O-*t-Butyldimethylsilyl*-2',3'-O-*isopropylidene*-β-D-*ribofuranosyl*)*maleimide* (**IIb**).—A solution of compound (**IX**) (0.10 g, 0.23 mmol) and pyridinium toluene-*p*-sulphonate (*ca.* 20 mg) in benzene (10 ml) was refluxed for 24 h, then concentrated and purified by flash chromatography using light petroleum–diethyl ether (1:1) as eluant. Compound (**IIb**)was obtained as an oil (47 mg, 53%), R_F 0.65 (diethyl ether), R_F 0.42 [diethyl ether–light petroleum (1:1)]; $\nu_{max.}$ 3 440, 3 250br, 3 030, 2 990, 2 960, 2 930, 2 860, 1 780, 1 730, 1 640, 1 475, 1 465, 1 385, 1 380, 1 350, 1 260, 1 160, 1 130, 1 080, 1 050, 970, 920, 860, and 835 cm^{-1}; $\delta_H(CDCl_3)$ 0.86 (9 H, s, SiBu^t), 1.36 and 1.58 (together 6 H, 2 s, CMe_2), 3.75 (2 H, dd, $J_{5',4'}$ 4 and 3.5 Hz, 5'-H_2), 4.24 (1 H, m, 4'-H), 4.72 (2 H, m, 2'- and 3'-H), 4.88 (1 H, dd, $J_{1',2'}$ 4 Hz, 1'-H), 6.54 (1 H, t, olefinic 3-H coupled with 1'-H and NH), and 7.9 (1 H, br s, NH). These spectra were identical in every respect with spectra of compound (**IIb**) supplied by Professor Just.

2-*Amino*-(5'-O-*t-Butyldimethylsilyl*-2',3'-O-*isopropylidene*-β-D-*ribofuranosyl*)-4H-*imidazol*-4-*one* (**X**).—Ozone was passed through a solution of compound (**Ib**) (0.387 g, 1 mmol) in methanol (25 ml) at −78 °C for 5 min. Excess of ozone was then removed in a stream of nitrogen before the addition of dimethyl sulphide (*ca.* 0.2 ml). The mixture was then stirred at 0 °C for 15 min prior to the addition of guanidine carbonate (0.198 g, 1.1 mmol) and potassium carbonate (0.116 g, 1.1 mmol). The mixture was stirred for 30 min at 0 °C, and for 1 h at room temperature, before evaporation under high vacuum at 30 °C. The residue was then resuspended in ethanol (10 ml) and afforded (after some time) a creamy white precipitate which was isolated by centrifugation, and then washed in succession with small volumes of ice-cold ethanol, water, ethanol, and finally diethyl ether. On being dried under high vacuum the product gave the microcrystalline *imidazolone* (**X**) [140 mg, 37% from (**Ib**)], m.p. 190 °C (decomp.); $\nu_{max.}$ 3 410, 3 250—3 130br, 1 670, 1 645, 1 600, 1 500, 1 270, 1 080, 830, and 780 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 0.85 (9 H, s, SiBu^t), 1.3 and 1.44 (together 6 H, 2 s, CMe_2), 3.55 (2 H, m, $J_{5',4'}$ 6 and 7 Hz, 5'-H_2), 3.98 (1 H, d, $J_{1',2'}$ 2.5 Hz, 1'-H), 3.80 (1 H, m, 4'-H), 4.46 (1 H, dd, $J_{3',2'}$ 7.5, $J_{3',4'}$ 4 Hz, 3'-H), and 4.92 (1 H, dd, $J_{2',1'}$ 2.5, $J_{2',3'}$ 7.5 Hz, 2'-H); *m/z* (32.9%) M^+, 383.1879 ($C_{17}H_{29}N_3O_5Si$ requires *M*, 383.1877).

Ethyl 5-(5'-O-*t-Butyldimethylsilyl*-2,3-O-*isopropylidene*-β-D-*ribofuranosyl*)-3,4-*dihydropyrazole*-5-*carboxylate* (**XI**).—To a solution of compound (**Ib**) (0.387 g, 1 mmol) in diethyl ether (10 ml) was added an ethereal solution of diazomethane (dropwise at 0 °C). When all starting material had been consumed, the solution was concentrated and the cycloadduct was purified by flash chromatography using light petroleum–diethyl ether (3:2) as eluant, to yield the title compound as an oil which crystallised with time (0.348 g, 81%), m.p. 54 °C; R_F 0.39 [light petroleum–diethyl ether (1:1)]; $\nu_{max.}$ 2 980, 2 960, 2 930, 2 860, 1 740, 1 560 (N=N), 1 475, 1 465, 1 380, 1 370, 1 260, 1 220, 1 160, 1 080, 890, 865, 835, 815, and 780 cm^{-1}; $\delta_H(CDCl_3)$ 0.1 (6 H, s, $SiMe_2$), 0.76 (9 H, s, SiBu^t), 1.2 (3 H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 1.22 and 1.45 (together 6 H, 2 s, CMe_2), 1.68 and 1.88 (together 2 H, 2 eight-line m, 3-H_2), 3.63 (2 H, dd, 5'-H_2), 3.9 (1 H, m, 4'-H), 4.22 (2 H, q, *J* 7 Hz, CO_2CH_2), 4.22 (1 H, m, 4-H), 4.4 (1 H, m, *J* 5 Hz, 2'-H), 4.48—4.62 (2 H br m, 3'- and 4-H), and 4.8 (1 H, d, *J* 5 Hz, 1'-H); *m/z* (5.9%) ($M^+ - C_4H_9$) 371.1616 ($C_{16}H_{27}N_2O_6Si$ requires *m/z* 371.1636).

Acknowledgements

P. D. K. thanks the S.E.R.C. for a studentship, and we thank Professor Just for spectra of compound (**IIa**).

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Received 8*th August* 1983; *Paper* 3/1383